

932,389



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PATENT SPECIFICATION

NO DRAWINGS

932,389

Inventors: JOHN EDWIN OAKLEY MAYNE,
HENRY WARSON, RALPH MANUEL LEVINE and
DONALD STEPHEN SOUTH

Date of filing Complete Specification: Aug. 18, 1960.

Application Date: Aug. 24, 1959.

No. 28918/59.

Complete Specification Published: July 24, 1963.

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Interns

ERRATUM

SPECIFICATION NO. 932,389

Page 1, heading, for "Classes 2(2)" read "Classes 2(6)"

THE PATENT OFFICE,
22nd November, 1963

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5 the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention is for improvement in or relating to polymer emulsions or dispersions and more particularly to polymer emulsions or dispersions based on homopolymers or copolymers of vinyl monomers and to the use thereof in surface coatings, adhesive compositions or as binders for animal, vegetable or mineral powder or fibres.

15 According to the invention there is provided a process for the manufacture of a polymer emulsion or dispersion which comprises polymerising, with the aid of a water-soluble polymerisation initiator, e.g., a peroxide or persulphate polymerisation initiator, one or more vinyl monomers in an aqueous medium containing a colloid obtained by the enzyme degradation of a natural starch, the enzyme-degraded starch having a reducing value of not more than 80 and the colloid being present in the proportion of 8% to 90% by weight of the vinyl monomer or monomers.

20 The vinyl monomers to be polymerised may be, for example, vinyl acetate, vinyl esters of higher homologues of acetic acid, or their copolymers may be made with alkyl esters of maleic or fumaric acid, and unsaturated fatty acids such as acrylic acid, methacrylic acid, crotonic acid or itaconic acid. Suitable starches, which after treatment with an enzyme yielded a useful colloid, include maize, waxy maize, farina, tapioca, wheat, rice, arrowroot, sorghum and waxy sorghum.

40 The enzymes which may be used to convert the parent starch into the colloid, include those

the products, which are odourless and virtually colourless, possess unusually high emulsifying and stabilising properties so that the final polymer emulsions or dispersions are extremely stable, and do not require the addition of other surface active agents and/or water-soluble colloids, before, during, or after polymerisation, to maintain stability.

50 The invention however, does not preclude the addition of anionic, cationic or nonionic surface active agents or water-soluble natural or synthetic colloids before, during, or after polymerisation. Furthermore, these additional materials may be added to modify the final emulsion properties.

55 We have found that the polymer emulsions or dispersions obtained by the process of this invention have properties which cannot be simulated by the post-addition, to an otherwise-prepared polymer dispersion, of either untreated starch, enzyme-degraded starch or any other starch derivative produced by such well-known means as dextrinisation, etherification, oxidation or chlorination. For example, the dispersed particles are of very fine size and their size may be readily controlled by variation of the enzyme-degraded starch/monomer ratio.

STARCH ENZYME-DEGRADATION STAGE

75 Starches, whether they be cereal, e.g. corn starch, or root starches, e.g. tapioca, differ from one another in first, the ratio of their amylopectin to amylose contents, and second, in the degrees of polymerisation and in the stereo-configurations of their amylopectin and amylose

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International Classification:—C08f. (C08b).

COMPLETE SPECIFICATION

Improvements in or relating to Polymer Emulsions or Dispersions

We, VINYL PRODUCTS LIMITED, a British Company, of Butter Hill, Carshalton, Surrey, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is for improvement in or relating to polymer emulsions or dispersions and more particularly to polymer emulsions or dispersions based on homopolymers or copolymers of vinyl monomers and to the use thereof in surface coatings, adhesive compositions or as binders for animal, vegetable or mineral powder or fibres.

According to the invention there is provided a process for the manufacture of a polymer emulsion or dispersion which comprises polymerising, with the aid of a water-soluble polymerisation initiator, e.g., a peroxide or persulphate polymerisation initiator, one or more vinyl monomers in an aqueous medium containing a colloid obtained by the enzyme degradation of a natural starch, the enzyme-degraded starch having a reducing value of not more than 80 and the colloid being present in the proportion of 8% to 90% by weight of the vinyl monomer or monomers.

The vinyl monomers to be polymerised may be, for example, vinyl acetate, vinyl esters of higher homologues of acetic acid, or their copolymers may be made with alkyl esters of maleic or fumaric acid, and unsaturated fatty acids such as acrylic acid, methacrylic acid, crotonic acid or itaconic acid. Suitable starches, which after treatment with an enzyme yielded a useful colloid, include maize, waxy maize, farina, tapioca, wheat, rice, arrowroot, sorghum and waxy sorghum.

The enzymes which may be used to convert the parent starch into the colloid, include those

amylases, e.g. α -amylase, commonly used to hydrolyse starch to dextrans. When the above-mentioned starches are suitably treated with the enzymes, the products, which are odourless and virtually colourless, possess unusually high emulsifying and stabilising properties so that the final polymer emulsions or dispersions are extremely stable, and do not require the addition of other surface active agents and/or water-soluble colloids, before, during, or after polymerisation, to maintain stability.

The invention however, does not preclude the addition of anionic, cationic or nonionic surface active agents or water-soluble natural or synthetic colloids before, during, or after polymerisation. Furthermore, these additional materials may be added to modify the final emulsion properties.

We have found that the polymer emulsions or dispersions obtained by the process of this invention have properties which cannot be simulated by the post-addition, to an otherwise-prepared polymer dispersion, of either untreated starch, enzyme-degraded starch or any other starch derivative produced by such well-known means as dextrinisation, etherification, oxidation or chlorination. For example, the dispersed particles are of very fine size and their size may be readily controlled by variation of the enzyme-degraded starch/monomer ratio.

STARCH ENZYME-DEGRADATION STAGE

Starches, whether they be cereal, e.g. corn starch, or root starches, e.g. tapioca, differ from one another in first, the ratio of their amylopectin to amylose contents, and second, in the degrees of polymerisation and in the stereo-configurations of their amylopectin and amylose

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sub-fractions. Hence, when treated by enzymes, the resultant colloids have different rheological properties.

5 For these reasons, certain of the above-mentioned starches are to be preferred. However, the enzyme-degradation process to be hereinafter described may be varied widely by altering the nature of the enzyme, ratio of
10 enzyme to starch, and the cooking time and temperature, so as to permit the formation of useful colloids from many starches.

Even a treated starch, e.g. dextrin, may be further treated by the action of enzymes to produce colloids suitable for the above-described emulsion polymerisation process.

15 It has been found, moreover, that pure amylopectin obtained by fractionating starch, e.g. farina (potato starch) can be enzyme-hydrolysed to yield a suitable colloid.

20 When an aqueous slurry of starch is heated to, or above, its gelation point in the presence of a starch-splitting enzyme, it gradually changes to a colloidal solution. During this process, the starch granules lose their botanical structure and the viscosity of the mixture falls as the process continues. In the first stage of the liquefaction, the swollen starch granules are disrupted with relatively little dextrinisation or formation of reducing groups. At a
30 later stage of the enzyme action, both the amylose and the amylopectin chains are broken into fragments with the formation of reducing groups. The formation of the reducing groups allows the reaction to be followed by an easy analytical technique, and at the same time suggests a method for controlling the process. The easy adjustment of the degree of conversion is one of the advantages of this process; others are the simple treatment involved
40 and the low cost of the raw materials.

It is possible, by an analytical method, to ascribe to the enzyme-degraded starch a "Reducing Value" as described in "Chemistry and Industry of Starch" by R. W. Kerr, Academic Press Inc., New York, 1950, Second Edition, pages 680—1. Untreated starch has a reducing value of the order of 1; fully hydrolysed starches have reducing values of the order of 300.

50 The Reducing Value, which is a measure of the degree of conversion, is proportional to the

quantity of enzyme used, the temperature of the treatment and the time of the treatment, provided the temperature, the pH and other conditions are so chosen that the rate of destruction of the enzyme activity is substantially less than the rate of hydrolysis of the starch by the enzyme.

It has been found that, for most starches, the useful Reducing Values lie between 10 and 30, although suitable polymer dispersions have been made based on enzyme-degraded starches with reducing values less than 10 and as high as 80. Most starches do not appear to liquefy until the Reducing Value is approximately 50 to 55 and for the preferred Reducing Values, when the starch has only been slightly degraded, it still retains much of its original botanical structure. This may be shown by observing the enzyme-degraded starch under a microscope fitted with polarising lenses, or by the blue-violet colouration with iodine; most true dextrins give a reddish-violet to reddish-brown colouration. The enzyme-degradation process is illustrated by the following description of a general method and by the following preparations, although the invention is not limited to these.

The aqueous enzyme solution is added to an approximately 25% by weight aqueous slurry of starch having a pH value of approximately 6.5, contained in a stainless steel jacketed-vessel fitted with a stirrer and open to the atmosphere via a reflux condenser.

The system is stirred at ambient temperature for 15—20 minutes to ensure good mixing and then, by means of jacket heating, the temperature of the mix is raised to the particular selected cooking temperature. This temperature is accurately maintained for the desired time, after which formic acid is added to lower the pH to just under 4. This destroys the activity of the enzyme, and so stops the starch conversion process. As soon as the formic acid has been added, the mix is cooled down to room temperature.

The Reducing Value and the viscosity of the particular enzyme-degraded starch depend on the time and temperature of the cooking process and also the quantity of enzyme present. The following examples illustrate this more clearly.

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In general, provided the conversion has not been carried to the point where the product is a clear, thin colloidal solution, the viscosity increases slightly over a period up to 48 hours after processing. This retrogression or "set-back", which is associated with the amylose portion of the starch used, does not affect the Reducing Value, and only very slightly affects the properties of the polymer emulsion.

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Preparation No. 1	Parts by Weight
{ Sorghum Starch 100%	100.000
{ Water 1	265.000
{ Enzyme powder (Nervanase 10X (Norman Evans & Rais Ltd)	0.350
{ Water 2	35.000
Formic Acid 90%	0.167

The word "Nervanase" is a Registered Trade Mark.

Water 1 is added to the vessel. Stirring is commenced and the starch is sprinkled in and stirred for 30 minutes at ambient temperature. The enzyme solution is added and the temperature is raised over a period of 15 minutes to 75°C. ± 1°C. The starch slurry has,

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Properties:
Reducing value
Viscosity
pH
Solids content
(theoretical)

20—30
2—7 poises at 25°C.
3.3—3.5
25%

PREPARATION No. 2
As in Preparation No. 1, but using waxy sorghum starch produced an opaque viscous dispersion having a Reducing Value of 31.4.

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PREPARATION No. 3
As in Preparation No. 1, but using maize starch produced an opaque dispersion having a Reducing Value of 36.2.

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PREPARATION No. 4
As in Preparation No. 3, but using 0.2 parts by weight of enzyme powder produced an opaque dispersion having a Reducing Value of 18.6.

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PREPARATION No. 5
As in Preparation No. 1, but using 0.1 parts of enzyme powder produced an opaque dispersion having a Reducing Value of 20.7.

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PREPARATION No. 6
As in Preparation No. 1, but using farina starch, cooking for 30 minutes at 70°C. produced an opaque dispersion having a Reducing Value of 25.

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at this point, a pH of approximately 6.5. This temperature is maintained for 30 minutes, and the formic acid is then added.

The resultant opaque dispersion is cooled to ambient temperature and is screened, before use, through 250 mesh nylon.

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PREPARATION No. 7
As in Preparation No. 6, but cooking for 90 minutes produced a cloudy colloidal dispersion having a Reducing Value of 58.1.

PREPARATION No. 8
As in Preparation No. 6, but cooking for 120 minutes produced a slightly cloudy colloidal dispersion having a Reducing Value of 65.2.

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PREPARATION No. 9
As in Preparation No. 6, but cooking for 150 minutes produced an almost clear colloidal solution having a Reducing Value of 77.3.

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PREPARATION No. 10
As in Preparation No. 3, but cooking for 120 minutes at 75°C. produced an almost clear colloidal solution having a Reducing Value of 76.6.

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PREPARATION No. 11
As in Preparation No. 1, but cooking for 120 minutes produced an almost clear colloidal solution having a Reducing Value of 78.7.

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EMULSION POLYMERISATION STAGE

The emulsion polymerisation may be carried out by a number of standard techniques familiar to those skilled in the art. The total monomer may be added to the water phase or it may be added portion-wise during the polymerisation, or preferably, it may be added slowly and continuously throughout the polymerisation.

In the preferred method of carrying out the polymerisation sufficient mild alkali, e.g. sodium bicarbonate, is added to a diluted suspension of enzyme-degraded starch to raise the pH to from 7 to 8. Using a water-soluble polymerisation initiator, e.g. potassium persulphate, the polymerisation may be completed by adding the monomer at a temperature of 70°—80°C. over several hours, after which the temperature is raised to 90°C. for a short time. After cooling the emulsion, the pH can be adjusted by the addition of aqueous caustic potash.

The proportion of enzyme-degraded starch to monomer greatly affects the properties of the polymer emulsion. In general, the greater the proportion of the enzymated starch, the higher is the emulsion viscosity and the finer is the particle size of the polymer.

Another result of increasing the proportion of enzyme-degraded starch to monomer is that the films deposited from the polymer emulsion become more water-sensitive. This disadvantage can easily be overcome by adding to the emulsions from 0.05% to 1.5% by weight of the emulsion of a dialdehyde such as glyoxal or dialdehyde starch.

Stable emulsions may be made using between 8 and 90% of solid enzyme-degraded starch by weight of the vinyl monomer. The preferred minimum quantity of enzyme-degraded starch for polyvinyl acetate homopoly-

mer emulsions of solid contents greater than 40% is 15%, since, below this quantity, the emulsion stability becomes impaired on plasticisation of the polymer to levels greater than 10% by weight.

The emulsion polymerisation process is illustrated by the following description of a general method and the following particular examples, although the invention is not limited to these.

To an aqueous dispersion of enzyme-degraded starch, prepared as described above, is added sufficient sodium bicarbonate to raise the pH to from 7 to 8. This mixture constitutes the aqueous phase of the emulsion.

The aqueous phase is added to a vessel similar to that described above in the enzyme-degradation process, and water is added to give a final emulsion solids content of 50% by weight. After stirring cold for 30 minutes, the temperature is raised to 60°C. when a portion of the total monomer is added, followed by the polymerisation initiator. By means of jacket heating, the internal temperature is raised to start the polymerisation and after a period of about 1 hour the temperature rises to 75°C.

At this point, the remaining bulk of the monomer is added slowly and continuously over several hours, during which time the temperature is maintained at 75°C. for only incipient reflux. Additional quantities of polymerisation initiator may be added.

When all the monomer has been added, the temperature is raised to 90°C. for 30 minutes. The emulsion may be then vented to the atmosphere to remove the last traces of residual monomer before being cooled.

The pH may then be adjusted with, for example, a dilute aqueous solution of potassium hydroxide.

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EXAMPLE No. 1

Formulation	Parts by Weight
{ Enzymated starch (100%)	15.00
{ Prepared according to Preparation 1	
Sodium bicarbonate	0.250
Water	to 50% solids content
Vinyl acetate monomer (1)	10.000
Potassium persulphate (1)	0.250
Vinyl acetate monomer (2)	90.000
Potassium persulphate (2)	0.125
Potassium persulphate (3)	0.125
Potassium hydroxide 25% solution	to pH 4.0 to 4.5

METHOD

5 The water phase ingredients are added to the vessel and stirred (250 r.p.m.) cold for 30 minutes. The temperature is raised to 60°C. when stage (1) monomer and polymerisation initiator are added.

10 The temperature is taken to 75°C. for no reflux. This should take 1—1½ hours.

Stage (2) monomer is added slowly and continuously for 3 hours during which time the temperature is maintained at 75°C. for only incipient reflux. Initiator stages (2) and

(3) are added at the beginning and at the end of the monomer addition respectively.

The temperature is raised to 90°C. for 30 minutes during which time there should be no reflux. The emulsion is then air blown for 20 minutes and cooled down in the usual manner.

The potassium hydroxide is added in very small portions—stirring for one hour between each portion until the final pH is reached.

The emulsion is finally screened through 250 mesh nylon.

General Properties

Solids content	50%
pH after addition of caustic potash	4.0—4.5
Viscosity, Ferranti VL/VM "C" (speed 5)	2—6 poises at 25°C. (thixotropic)

EXAMPLE No. 2

30 In this example, the monomer is a mixture of 3 parts by weight of vinyl acetate to 1 part by weight of vinyl caprate so that the resultant emulsion deposits films which are inherently flexible and do not require the further addition of a plasticiser. The process is as Example No. 1 except that the enzyme-degraded starch was prepared according to Preparation No. 6 above.

EXAMPLE No. 3

As Example No. 1 but increasing the percentage of enzyme-degraded starch by

weight of monomer from 15% to 30%. This resulted in a highly viscous emulsion of very fine particle size. This emulsion is extremely thixotropic.

EXAMPLE No. 4

45 114 gm of amylopectin "G" produced by Avebe, of Veendam, Holland, derived from farina starch (dry weight 100 gm) was sprinkled into sufficient water to form a 25% by weight solids dispersion. The enzyme had previously been added to the water in an amount of 0.35% by weight of the amylopectin and the treatment of enzyme-degradation

was carried out at 75°C. until a Reducing Value of 19.5 was attained at which point enzyme action was stopped by the addition of formic acid.

5 The treated amylopectin solution was then used in the production of a polymer emulsion as described in Example 1.

10 The various polymer emulsions and dispersions produced in accordance with the process of the present invention may readily be plasticised by stirring the desired plasticiser, e.g. dibutylphthalate or di-isobutyl phthalate, into the emulsion at room temperature, without the necessity of adding any additional water; amounts of plasticiser up to 30% by weight of the solids content of the emulsion or dispersion can very easily be incorporated in this way.

15 The emulsions and dispersions produced by the process of the present invention may be used for a wide variety of purposes amongst which may be mentioned the back-sizing of carpets, use as adhesives and use as the basis of coating compositions such as water-based synthetic resin paints.

WHAT WE CLAIM IS:—

1. A process for the manufacture of a polymer emulsion or dispersion which comprises polymerising, with the aid of a water-soluble polymerisation initiator, e.g. a peroxide or persulphate polymerisation initiator, one or more vinyl monomers in an aqueous medium containing a colloid obtained by the enzyme degradation of a natural starch, the enzyme-degraded starch having a Reducing Value of not more than 80 and the colloid being present in the proportion of 8% to 90% by weight of the vinyl monomer or monomers.

2. A process according to claim 1 wherein the vinyl monomer is vinyl acetate.

3. A process according to claim 1 or claim 2 wherein the enzyme-degraded starch has a Reducing Value of between 10 and 30.

4. A process according to any of the preceding claims wherein the aqueous medium containing the vinyl monomer or monomers is heated to a temperature of 70° to 80°C.

5. A process according to any of claims 2 to 4 wherein the enzyme-degraded starch is used in an amount of at least 15% by weight of the vinyl acetate.

6. A process according to any of the preceding claims wherein there is added an amount of from 0.05% to 1.5% by weight of the emulsion or dispersion of a dialdehyde.

7. A process according to any of the preceding claims wherein the emulsified or dispersed polymer or copolymer is plasticised by stirring a plasticiser into the emulsion.

8. A process according to claim 7 wherein the plasticiser is employed in an amount up to 30% by weight of the solids content of the emulsion or dispersion.

9. The process for the manufacture of an emulsion or dispersion of a vinyl polymer or copolymer substantially as described in any of the Examples 1 to 4.

10. Emulsions and dispersions of vinyl polymers and copolymers when prepared by the process claimed in any of the preceding claims.

11. Adhesive compositions and surface coating compositions comprising an emulsion or dispersion claimed in claim 10.

STEVENSON, LANGNER, PARRY
& ROLLINSON,
Chartered Patent Agents,
Agents for the Applicants.